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(54) Name of the invention:

Manufacturing Method for Crystallized Glass

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Description of the invention

1. Name of the invention

Crystallized Glass Manufacturing Method

2. Scope of the Claims

- (1) Crystallized glass manufacturing method where a glass material is obtained as a crystallized glass component, formed as, by weight %, SiO_2 : 5 ~ 50 %, Al_2O_3 : 5 ~ 70 %, Y_2O_3 : 10 ~ 70 % are contained as the main components, and among the MgO , TiO_2 , ZrO_2 , La_2O_3 etc., additive agents, at least one type or more is contained as a seed forming agent, is melted and slowly cooled, or as the molten solution is rapidly cooled; and this glass material is then subjected to a thermal treatment at a temperature in the range of 900 ~ 1250°C for a period that is within 100 hours, and by that micro-crystals are separated.
- (2) Crystallized glass manufacturing method where in order to mix homogeneously the powder material with the composition according to the above Claim paragraph (1), relative to 100 weight parts of the raw material component fine powder material with an average particle diameter in the range of 0.1 ~ 300 microns, as a solvent media, water or organic solvent is added in an amount that is in the range of 20 ~ 150 weight parts, and in order to homogeneously disperse the powder, water soluble acrylic resin, polyethylene glycol, polyethylene amine, anionic type polymer etc., organic material component is added in an amount in the range of 0.1 ~ 10 weight parts, and the mixed ceramics powder is homogeneously mixed and dispersed, and after that the solvent agent is evaporated and a homogeneously mixed powder is obtained, and this is heated to a temperature in the range of 300 ~ 700°C, and the resin is eliminated, and after that it is melted at a high temperature and it is slowly cooled or the molten solution is rapidly cooled, and the obtained by that glass material is then subjected to a thermal treatment at a temperature in the range of 900 ~ 1250°C for a period that is within 100 hours, and by that micro-crystals are separated.

3. Detailed Description of the Invention

[Technological Field of Application]

The present invention is an invention about the manufacturing method for the production of crystallized glass with high hardness and with excellent heat resistance and corrosion resistance properties. And especially, the present invention is an invention about the manufacturing method for the production of the same glass that can be effectively and appropriately used in the manufacturing of heat resistant, wear resistant ceramics dials or ceramics substrate plates, containers, etc.

[Previous Technology]

The manufacturing method for the production of the glass according to the previous technology is simple, however, there has been the drawback that at high temperatures of several hundreds of degrees Celsius and above, it undergoes softening, etc. Among these materials, the glass materials containing SiO_2 , Al_2O_3 , Y_2O_3 as their main components have a melting point of approximately 1350°C and higher, and they can be used as a glass material up to relatively high temperatures, however, even in the case of these materials, there has been the drawback that at temperatures of 900°C and above, there is softening. On the other hand, alumina, etc., sintered materials then can be used at high temperatures, however, it is necessary that they be sintered at high temperatures of 1700°C, and there is the drawback that the cost becomes high.

[Problem Points Solved by the Present Invention]

The present invention has taken into consideration the above described technology references, and it is an invention that is suggesting a method for the preparation of crystallized ceramics material, where in order to decrease the effect of the softening of the glass at high temperature, fine crystals of alumina, garnet etc., are separated in large amounts, and through that the heat resistance properties obtained are high and this material can be used even at relatively high temperatures of several hundred degrees C; and also, where the raw material powder is finely pulverized and it is homogeneously mixed in advance and by that the time period of the homogenization heat treatment of the molten solution at a high temperature is made shorter, and as the high temperature technological process is made shorter compared to the glass manufacturing method according to the previous technology, a method for obtaining crystallized ceramics material with homogeneously dispersed fine crystals, is suggested. Also, in order to separate a large amount of fine crystals, usually, it is necessary to generate a large number of crystal seeds (nuclei), and because of that through the addition of additive agents that are materials, which easily become crystalline nuclei for crystalline growth, it is an invention that suggests a method for the promoting of the glass crystallization.

Because of that, the present invention is an invention that produces ceramics with different types of compositions, and that first practically investigates the composition

range of the region where the necessary for the generation of crystallized glass, unknown up to now, high temperature solid phase and a liquid phase co-exist, and then it is an invention that clarifies the conditions for the crystallization of the glass phase.

[Measures in Order to Solve the Problems]

The present invention is a crystallized glass manufacturing method where a glass material is obtained as a crystallized glass component, formed as, by weight %, SiO_2 : 5 ~ 50 %, Al_2O_3 : 5 ~ 70 %, Y_2O_3 : 10 ~ 70 % are contained as the main components, and among the MgO , TiO_2 , ZrO_2 , La_2O_3 etc., additive agents, at least one type or more is contained as a seed forming agent, is melted and slowly cooled, or as the molten solution is rapidly cooled; and this glass material is then subjected to a thermal treatment at a temperature in the range of 900 ~ 1250°C for a period that is within 100 hours, and by that micro-crystals are separated. And also, the present invention is a crystallized glass manufacturing method where in order to mix homogeneously the powder material with the composition according to the above Claim paragraph (1), relative to 100 weight parts of the raw material component fine powder material with an average particle diameter in the range of 0.1 ~ 300 microns, as a solvent media, water or organic solvent is added in an amount that is in the range of 20 ~ 150 weight parts, and in order to homogeneously disperse the powder, water soluble acrylic resin, polyethylene glycol, polyethylene amine, anionic type polymer etc., organic material component is added in an amount in the range of 0.1 ~ 10 weight parts, and the mixed ceramics powder is homogeneously mixed and dispersed, and after that the solvent agent is evaporated and a homogeneously mixed powder is obtained, and this is heated to a temperature in the range of 300 ~ 700°C, and the resin is eliminated, and after that it is melted at a high temperature and it is slowly cooled or the molten solution is rapidly cooled, and the obtained by that glass material is then subjected to a thermal treatment at a temperature in the range of 900 ~ 1250°C for a period that is within 100 hours, and by that micro-crystals are separated.

[Effect]

Regarding the glasses that have Al_2O_3 , Y_2O_3 , SiO_2 as their main components, and that do not contain Na, K, etc., alkali metals, compared to the usual alkali glass materials, they have the characteristics where it is said that both the softening point temperature and the melting point temperature, are high, however, in order to improve the heat resistant properties and the hardness, etc., properties, it is necessary that a large amount of high hardness alumina Al_2O_3 or garnet $\text{Al}_5\text{Y}_3\text{O}_{12}$, etc., be separated. Because of that, through the optimization of the composition range of the main components, the added amount of the seeding agents, the method for the mixing of the fine raw material powder material, it has been possible to achieve the desired goals. Here below, an explanation regarding these effects will be provided.

- (1) As main components, as weight %, SiO_2 : 5 ~ 50 %, Al_2O_3 : 5 ~ 70 %, Y_2O_3 : 10 ~ 70 %, are contained. In the case of the compositions outside of these ranges, there is no formation of glass, or because the amount of the generated liquid phase that is in a co-existence state with the high temperature solid solution is extremely

small, there is only a generation of sintered material, and because of that there is the drawback that even if it is heated at a high temperature of up to 1700°C no experimental material is obtained. Moreover, even within this compositional range, in order to separate a large amount of alumina or garnet etc., crystals, especially, it is necessary to select the concentration of the SiO₂ to be within the range of 5 ~ 30 %.

- (2) As the seeding agents, at least one type or more of MgO, TiO₂, ZrO₂, La₂O₃, etc., oxide materials is added in an amount in the range of 0.1 ~ 30 %. In the case when the added amount is less than 0.1 %, there is no crystallization promoting effect at all, and also, in the case when the amount added exceeds 30 %, the problems appears that also because of the crystallization promoting effect, the melting point also becomes low, and that is why these options are not preferred. Also, because of the fact that with the increase of the number of types of the additive agents, the glass melting point is decreased, it is preferred that if possible the number of types of the seeding agents, be kept at one. Moreover, the fact that the effect of the seeding agent is due to the strong trend that the additive agent is dissolved in the glass and a multi-element type solid solution is formed, and through a crystallization thermal treatment, the glass is microscopically phase separated and by that the separation of Al₂O₃, or Al₅Y₃O₁₂ etc., crystals, is promoted, will be confirmed by the described her below practical implementation examples.
- (3) The crystallization thermal treatment is conducted as the material is heated at a temperature that is in the range of 900 ~ 1250°C, and this is maintained for a period that is within 100 hours. In the case when there is no addition of a seeding agent, the crystallization occurs at a temperature approximately in the range of 1000 ~ 1270°C, however, if a seeding agent is added, the crystallization can be conducted at a lower temperature. Also, it is a good option if the duration of the thermal treatment is within 100 hours. The reason for that is that by only heating at this temperature, the crystallization proceeds partially, and also, that by a thermal treatment with a duration within 100 hours, the crystallization is completed, and even if it is heat treated beyond that, the degree of crystallization is not increased. Moreover, in order to promote the crystallization, the method where the glass is again heated at high temperature, and besides that method, whereby the heated and melted at a high temperature molten solution in an electric kiln is slowly cooled at a rate of 20°C/min, or less, lead to the same results.
- (4) The technological process used in order to homogeneously mix the fine raw material powder, has the described below results. The particle diameter of the raw material powder is made to be within the range of 0.1 ~ 300 microns. In the case of particles that are smaller than that, the cost of the fine and ultra-fine particles is high, and also, in the case of large particles with a diameter larger than that, longer time is required for melting in order to achieve homogeneous material during the melting of the glass, and because of that such size are not appropriate.

Preferably, powders with submicron particle diameter are used, and by that, it is possible to shorten the melting time during the manufacturing process. Relative to 100 weight parts of the raw material powder, solvent agent is added in an amount in the range of 20 ~ 150 weight parts, and an organic material is added in an amount in the range of 0.1 ~ 10 weight parts. In the case when the amount of the solvent agent is less than 20, the flow properties of the mixed material are not good, and also, even when solvent amount in excess of 150 is added, the mixed material is already in a suspension state and then the further addition of a solvent medium is not necessary. Regarding the organic material, any material is a good option as long as it has a dispersing effect relative to the powder materials used as the main components, and regarding the added amount, if it is less than 0.1, the effect is small, and also, if it is more than 10, the time for the removal of the resin becomes long, and there is the problem that it is said that the amount added is higher than the required amount. It is preferred that the technological process of the mixing of the raw material powder is done according to the described here below.

- (5) If the obtained, organic material component containing mixed powder material is heated in the atmosphere or under reduced pressure, at a temperature in the range of 300 ~ 700°C, the organic material component is destructed and transformed into a gas phase and because of that the resin is removed, or regarding this process, it is also a good option if the powder material is heated inside an electric kiln, and the removal of the organic material is made to be one part of the melting technological process, and thus it is not necessary to define a specific resin removal technological process. Also, regarding the heating and melting conditions for the powder material, for example, it is a good option if it is heated at a temperature that is in the range of 1300 ~ 1500°C, for a period in the range of 0.1 ~ 5 hours, in an alumina kiln container. In order to generate glass material, it is necessary that a liquid phase is present at a high temperature, and because of that regarding the heating temperature, there are no specific limitations required as long as it is said to be a temperature where a molten solution is present. Moreover, in the case when the used solvent medium is water, as an organic material component, it is a good option to use water soluble acrylic resin, anionic type polymer, etc., and if the solvent medium is an organic solvent medium, it is possible to use soluble in the solvent medium polyethylene imine, etc., polymer material or a surface active agent. Moreover, from a cost point of view, the method where water is used for the dispersing process is preferred because of its low cost.

[Practical Examples]

As one practical implementation example of the present invention, an example regarding a manufactured crystallized glass example is explained here below.

A mixed powder material where relative to 100 weight parts of raw material powder with a composition defined as it is shown according to Table 1, and with a submicron particle

diameter, 50 weight parts of water, and 2 weight parts of anionic type polymer, are added, and this is mixed in a container for 20 hours, and a powder material where as the solvent 100 weight parts of ethanol are added, and 2 weight parts of polyethylene amine (this is amine, and above it was imine, could also be a typo – Translator's note) are added, and mixed for 20 hours, and powder materials were produced.

These powder materials were heated at a temperature of 500oC and at a vacuum of 0.1 Torr for a period of 1 hour, and after that, through the observed results from the variation of the diffraction intensity of the powder material measured by X-ray diffraction method, it was confirmed that the powder material was homogeneously mixed.

This mixed powder materials were placed inside alumina kiln containers, an as a temperature of 1500oC was maintained, they were heated for a period of 1 hour, and after that they were rapidly cooled, and the obtained glass materials were heat treated at a temperature of 1100oC for a period of 2 hours, and the crystallized glass materials shown according to Table 2, were obtained.

Moreover, as another practical implementation example, the Experimental material 4 was heated at a temperature of 1500oC for 1 hour and melted, and after that it was slowly cooled at a rate of 10oC/min, and by that it was possible to obtain the same white color crystallized glass material.

As it is shown according to Table 2, it was observed that in the case when a seeding agent was added, the crystallization initiation temperature of the glass phase that was obtained through the rapid cooling of the solid solution co-existence state (Experimental materials 4, 5 and 6) became lower compared to the experimental materials where there was no addition of seeding agents (8), and because of that, it was understood that MgO, TiO₂, ZrO₂, etc., oxide materials are effective in promoting the crystallization. Moreover, according to the method used in the previous technology, in the case when glass has been synthesized from powder material with a particle diameter of 100 microns, in order to produce homogeneous glass material, it has been necessary to maintain the material for a long time at the molten state, however, if the submicron level fine powder material is pre-dispersed in advance, even if it is heated at a temperature of 1500oC for a period of only 0.1 hours, a sufficiently homogeneous glass is obtained, and it was understood that the results of the present invention have a large effect on the used fine raw material powders. The glass transition point temperature of the obtained glass is approximately 900oC, however, through the separation of a large amount of crystals it is possible to increase the crystallization temperature to approximately 1000oC, and it is understood that a simple method is discovered whereby through only a simple heating in an electric kiln, high thermal resistance, and high hardness ceramics materials are obtained. Moreover, there is an amount of SiO₂ inside the glass, however, it was understood that by making the amount of the SiO₂ in the range of 30 ~ 50 %, crystalline SiO₂ is separated inside the glass, and on the top of that, it is connected to the vitrification region. Also, in the case of glasses with different types of compositions, it was judged that in order to have a separation of fine crystals of high hardness Al₂O₃ or Al₅Y₃O₁₂, the concentration of the SiO₂ must be at or below 30 %.

Table 1**Composition of the Raw Material Powder and Powder Preparation Conditions**

(The concentration is in weight %, the compounded amounts are shown as values relative to 100 weight parts of the ceramics powder material.)

Experimental Material Number	SiO ₂ Conc.	Al ₂ O ₃ Conc.	Y ₂ O ₃ Conc.	Seeding Agent Conc.	Solvent Compounded Amount	Organic Material Compounded Amount
1	24	42	29	ZrO ₂ :5	Water:50	Anion type polymer:2
2	19	47	29	"	"	"
3	"	"	"	"	Ethanol:100	Polyethylene amine:2
4	19	29	47	ZrO ₂ :5	Water:50	Anion type polymer:2
5	"	"	"	MgO:5	"	"
6	"	"	"	TiO ₂ :5	"	"
7	19	24	53	ZrO ₂ :4	"	"
8	20	30	50	Not added	"	"

Table 2**Conditions of the Preparation of the Crystallized Glass and Properties**

(The melting conditions are 1 hour at 1500°C)

Experimental Material Number	Crystallization Heat Treatment	Separated Main Crystals	Crystallization Initiation temperature (°C)	Vickers Hardness (Gpa)
1	1100°C, 2 hr	A, M	950	8.3
3	"	A, G	1000	8.5
4	"	G, YS	960	8.5
5	"	"	940	8
6	"	"	950	8.3
7	"	YS, G	950	10
8	"	G, YS	1010	7.5

(Results From the Invention)

By using fine powder material as the raw material and by adding a seeding agent, it is possible to manufacture a high thermal resistance and high hardness crystallized glass material, and it has high merits from the point of view of the technological sphere of wear resistant parts that can be used at high temperatures, etc. Within the present invention, especially, due to the crystallized glass manufacturing utilizing the homogeneous dispersing of the fine powder material in advance, there is also the result that glass melting technological process becomes simple etc., and that leads to a decrease of the manufacturing costs, and then, in the case of this crystallized glass material, there is no alkali, and compared to the usual alkali glass, it is chemically stable, and the durability properties relative to corrosive ambient environments, are also increased.

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